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Study in Optical and Mechanical Properties of Nd³⁺, Y³⁺: SrF₂ Transparent Ceramics Prepared by Hot-Pressing and Hot-Forming Techniques

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Abstract: Nd^{3+} , Y^{3+} : SrF_2 transparent ceramics were successfully synthesized by two methods: hot-forming and hot-pressing techniques. The mechanical properties and optical properties of the hot-formed Nd^{3+} , Y^{3+} : SrF_2 transparent ceramics were much better than that of single crystal. On the other hand, the transmittance of the hot-formed transparent ceramics with different deformation rate reached up to 90% at 1054 nm, which is superior to the hot-pressed ceramics. Furthermore, the fracture toughness of hot-formed Nd^{3+} , Y^{3+} : SrF_2 transparent ceramics with the deformation rate of 51% reached up to 0.70 MPa m^{1/2}, which is nearly 1.5 times higher than that of as-grown single crystal. The full width at half maximum (FWHM) of the hot-formed ceramic is larger than that of the single crystal at 1053 nm under continuous-wave (CW) laser operation. The thermal conductivity of Nd^{3+} , Y^{3+} : SrF_2 single crystal and hot-formed ceramics were also discussed.

Keywords: Nd³⁺, Y³⁺: SrF₂ transparent ceramics; hot-forming; hot-pressing

1. Introduction

Since the first fluoride laser ceramic Dy^{2+} : CaF_2 was synthesized by hot-pressing powders in the 1960s [1], fluoride laser ceramics have become popular during recent decades. Compared to oxide laser ceramics [2,3], fluoride laser ceramics have some unique advantages, such as wide range of light transmission [4], low phonon energy, stable chemical properties [5], low melting point and low reflective index [6]. Usually, the transparent ceramics are prepared by spark plasma sintering (SPS) and hot-pressing. Due to the low sintering temperature and short holding time, SPS has been applied in the preparation of thermoelectric materials [7,8], optical materials [9], and other inorganic functional materials [10]. Shi Chen prepared CaF_2 ceramic by SPS in 2014 [11], and investigated the influence of temperature on SPS. Furthermore, Fumiya Nakamura prepared CaF_2 transparent ceramics by SPS, whose thermally stimulated luminescence was much stronger than that of the single crystal sample [12]. However, these CaF_2 transparent ceramics had low optical quality. Recently, B.C. Mei and co-workers used a hot-pressing technique to prepare a series of high-quality fluoride transparent ceramics, such as Er, Na: CaF_2 [13], Nd: CaF_2 [14], and $Er: CaF_2$ [15]. A. Lyberis prepared Yb: CaF_2 laser ceramics which transmittance was higher than 97% [4]. However, these laser ceramics exhibited low efficiency of laser output, and even failed to achieve laser output because of the defects and impurities in laser ceramics.



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In order to address the inferior optical quality of the fluoride laser ceramics, a new facile method for preparing fluoride laser transparent ceramics has been developed, involving deformation of the single crystal structure into polycrystalline by a hot-forming method, which avoids the formation of crystal defects during powder sintering, maintaining the excellent optical quality of single crystals and, at the same time, improving the mechanical properties. In 2008, T. T. Basiev synthesized $CaF_2-SrF_2-YbF_3$ laser ceramics by deforming single crystals. The laser performance of the as-synthesized laser ceramics is similar to single crystal with the same component while the fracture toughness is 1.75 times higher than that of single crystal [16]. Thereafter, Yb^{3+} : CaF_2 ceramics [17], Nd^{3+}: SrF_2 [18], Tm: CaF_2 [19], and Er^{3+} : CaF_2 [20] hot-formed transparent ceramics were also prepared by deforming single crystal. However, there have not been any studies into fabrication nor investigation of the optical and mechanical properties of the hot-formed laser ceramics with different deformation rate, hot-pressed laser ceramics prepared by nano-powder, and single crystal with the same component.

In this paper, Nd^{3+} , Y^{3+} -doped SrF_2 laser ceramics were synthesized by two methods: hot-forming and hot-pressing techniques. The optical and mechanical properties of the hot-formed laser ceramics at different deformation rate, hot-pressed laser ceramics prepared by sintering the nano-powder, and single crystal with the same component were explored for the first time. Compared with the single crystal, the hot-formed ceramic exhibited better laser performance during continuous-wave (CW) laser operation, making it a promising candidate for high-power laser devices.

2. Experimental Section

Single crystals of 0.5 at.% Nd^{3+} , 5 at.% Y^{3+} : SrF_2 were prepared by a temperature gradient technique (TGT) method [21]. The 0.5 at.% Nd^{3+} , 5 at.% Y^{3+} : SrF_2 transparent ceramics were prepared by two methods: hot-pressing and hot-forming techniques. The hot-pressing technique was based on sintering polycrystalline powder at high pressure, as shown in our previous report [22]. The hot-formed ceramics were fabricated by deforming the single crystals in vacuum at different deformation rate by controlling the vertical pressure. The detail forming procedures as follows: the sintering temperature raised from room temperature to 1150 °C with heating rate of 3 °C/min, while a vertical pressure between 0.5 to 1.5 t was applied on the single crystal for 20 min at 1150 °C. Subsequently, the vacuum furnace was cooled down to 500 °C with cooling rate of 3 °C/min and then quenched to room temperature. The as-synthesized samples were both polished, and the thickness of all the samples were around 3 mm, as shown in Figure 1.



Figure 1. Photograph of the Nd³⁺, Y³⁺: SrF₂ hot-formed ceramics at different deformation rate, (a) $\Delta a = 26\%$; (b) $\Delta a = 45\%$; (c) $\Delta a = 51\%$; (d) $\Delta a = 68\%$.

The crystal structure of transparent ceramics and single crystal were investigated by X-ray diffraction (XRD, D/MAX-RB, RIGAKU, Japan). The microstructure of the single crystal and transparent ceramics was observed using a field-emission scanning electron microscope (ULTRA PLUS-43-13, Zeiss,

Oberkochen, Germany). The transmittance spectra were obtained by an ultraviolet/visible/near-infrared spectrophotometer (Lambda 750 S, Perkin Elmer, MA 02420, USA) between 200 and 1200 nm.

Calculations of the deformation rate exhibited as follows:

$$\Delta a = \frac{H_1 - H_2}{H_1} \times 100\%$$

where H_1 and H_2 are the height of Nd³⁺, Y³⁺: SrF₂ samples before and after plastic deformation process respectively.

The microhardness and fracture toughness of the hot-formed ceramics, hot-pressed ceramics, and the same-component single crystals were measured by a digital display Vickers hardness tester (402MVD, Wilson, Illinois, WI, USA). Indentation was performed using a microhardness meter. The microhardness was calculated according to the following formula:

$$H = K \frac{P}{d^2}$$

where *P* is the indentation load on the sample; *d* is the length of indentation diagonal; and *K* is the factor depending on the shape of the indenter. In this paper, *K* is equal to 1.854.

The fracture toughness is determined from the linear sizes of radial cracks (C) arising near the point of load application. It was calculated based on the following formula:

$$K_{1C} = \frac{0.016 \left(\frac{E}{H}\right)^{\frac{1}{2}}}{C^{\frac{3}{2}}} \times P$$

where *H* is the microhardness, *P* is the load, and *E* is the Young's modulus. In this paper, a universal material testing machine (MTS-810, MN, USA) was used to measure the Young's modulus. For hot-formed ceramic, E = 86.73 GPa. For hot-pressed ceramic, E = 87.48 GPa. For single crystal, E = 79.30 GPa.

CW laser measurement was realized by laser diode (LD) pumping the hot-formed sample, which the central wavelength was around 796 nm. The double-side polished samples were processed to 3 mm \times 3 mm \times 5 mm. The physical length of the cavity was 184 mm. The focusing system was used to deliver the pump light to the laser medium whose focal radius was 800 µm. The oscillation spectrum was investigated by a spectrum analyzer, whose test deviation is ±0.1 nm. The laser medium was installed in a water-cooled copper block to remove the heat and which maintains the temperature at 13 °C.

Calculations of the thermal conductivity K as follows:

$$K = \alpha \rho C_P$$

where ρ is density of samples. The α is the thermal diffusivities obtained by the laser flash apparatus (LFA457, Netzsch, Bavaria, Germany) and Cp is specific heat of samples, which was measured by microcalorimeter (C80, SETARAM, France).

3. Result and Discussion

Figure 2 shows the X-ray diffraction patterns of the 0.5 at. % Nd³⁺, 5 at. % Y³⁺: SrF₂ single crystal, hot-pressed ceramics prepared by sintering the nanopowders, and the hot-formed ceramics with different deformation rate. For the single crystal, there is only (111) peak revealed in the XRD pattern. The diffraction pattern of the hot-pressed ceramics prepared by nanopowders is well corresponding to the pure SrF₂ phase (PDF: No.06-0262). For the hot-formed ceramics based on single crystal, the number of X-ray diffraction peak increased with the raising deformation rate from 26% to 51%, which indicates that the single crystal successfully transferred into the polycrystalline by plastic

deformation. When the deformation rate reaches to 51%, there are four diffraction peaks shown in the XRD pattern corresponding to the (111), (220), (311), and (331) plane, which can be assigned to the SrF_2 perfectly without any impurities. The change of the number of diffraction peak can be explained as follows: SrF_2 possesses five independent slip systems, each independent slip system has its minimum slip driving forces [23]. With the temperature and pressure increased, the slip system that possessed minimum energy was first activated, then the diffraction peak occurred. Since the slip systems were activated one by one with increasing pressure, the number of diffraction peaks increased. On the other hand, the crystallographic planes of hot-formed ceramic rotated by large angle with the increase of the deformation rate [24]. When the deformation rate was further increased, the block with crystallographic planes was distributed and the new plane was formed, which acquired the lowest energy. Therefore, it can be observed the number of the diffraction peak of the ceramics with the deformation rate of 68% is less than that of the ceramic with the deformation rate of 51%.



Figure 2. XRD patterns of the Nd^{3+} , Y^{3+} : SrF_2 hot-pressed ceramics, single crystal, and the hot-formed ceramics at different deformation rate.

Figure 3 shows the SEM images of the fracture surface of the single crystal, hot-pressed ceramic, and hot-formed ceramic. For single crystal, there are no grain boundaries, but some point defects were revealed, as shown in Figure 3a. The fracture surface of hot-pressed ceramics was exhibited in Figure 3b. The grain boundaries were clearly observed, and the grain size of the ceramics was between 200 and 300 nm. However, some pores existed between the grains. The fracture surface micrographs of the hot-formed Nd³⁺, Y³⁺: SrF₂ ceramics at deformation rates of 26%, 45%, 51%, and 68% are shown in Figure 3c–f, respectively. It is obviously shown that the hot-formed ceramics exhibited layered structure that thickness of each layer is between 100 and 200 nm. With the increase of the deformation rate, the number of the layer was gradually increasing. This change can be assigned to that under high temperature and pressure, the original single crystal was destroyed and slides to different orientations, resulting in a layered structure, which is similar to the XRD results. The microstructure of hot-formed ceramics has less defects than that of the hot-pressed ceramic, which might be reason for the higher transmittance than that of the hot-pressed ceramics.

The microhardness and fracture toughness of the Nd^{3+} , Y^{3+} : SrF_2 single crystal, hot-pressed ceramics and hot-formed ceramics with different deformation rate are presented in Table 1. It is clearly revealed that hot-pressed ceramics possessed higher microhardness and fracture toughness than that of single crystal and hot-formed ceramics with the same composition. Generally, the grain size and grain boundaries of the transparent ceramics have a significant influence on the mechanical properties. The small grain size and large grain boundary areas can distribute external stress and hinder microcrack propagation effectively, then improving the microhardness the fracture toughness. That is the main

reason why the mechanical properties of hot-pressed ceramics are better than that of hot-formed ceramics. The fracture toughness of the Nd^{3+} , Y^{3+} : SrF_2 hot-formed ceramics increased at first and then decreased with the increase of deformation rate. When the deformation rate reached up to 51%, the fracture toughness obtained the maximum value with 0.70 MPa m^{1/2}, which is nearly 1.5 times higher than that of as-grown single crystal. This phenomenon can be explained as follows: With the increase of the temperature and pressure, the grain boundaries were formed during the transformation from single crystal to polycrystal, which is beneficial in improving the fracture toughness of ceramics. However, when the deformation rate reached up to 68%, the fracture toughness of ceramics decreased slightly compared with that of 51%, which may be due to secondary recrystallization in localized areas at higher deformation rate, similar to the deformation of LiF single crystal [25].



Figure 3. FE-SEM images of (**a**) Nd^{3+} , Y^{3+} : SrF_2 single crystal, (**b**) Nd^{3+} , Y^{3+} : SrF_2 hot-pressed ceramics, (**c**-**f**) Nd^{3+} , Y^{3+} : SrF_2 hot-formed ceramics with different deformation rate.

Table 1. The microhardness and fracture toughness of the Nd^{3+} , Y^{3+} : SrF_2 single crystal, hot-pressed ceramic and hot-formed ceramics at different deformation rate.

Material Type	Microhardness H (GPa)	Fracture Toughness K_{1C} (MPa m ^{1/2})
hot-formed ceramic ($\Delta a = 26\%$)	2.645	0.51
hot-formed ceramic ($\Delta a = 45\%$)	2.520	0.55
hot-formed ceramic ($\Delta a = 51\%$)	2.570	0.70
hot-formed ceramic ($\Delta a = 68\%$)	2.433	0.60
hot-pressed ceramic	2.680	0.80
Single crystal	2.245	0.48

The measured density and relative density of the Nd³⁺, Y³⁺: SrF₂ single crystal, hot-pressed ceramics and hot-formed ceramics ($\Delta a = 51\%$) are exhibited in Table 2. It is clearly revealed that the

hot-pressed ceramics have lower density than that of the hot-formed ceramics, which can be attributed to the different sintering techniques. In hot-pressed process, even though the rapid growth of grains removed the pores greatly, a few residual pores still remain in the ceramics, which affect the density of the transparent ceramic [26]. This result can be confirmed in Figure 3b). By contrast, the hot-formed process deforms the single crystals in vacuum without powder sintering, which avoids the formation of the pores and impurities. It is beneficial for improving the density of the transparent ceramics. In addition, a high density is helpful for improving the transmittance of the ceramics.

Table 2. The measured density and relative density of the Nd^{3+} , Y^{3+} : SrF_2 single crystal, hot-pressed ceramic, and hot-formed ceramics.

Material Type	Measured Density (g/cm ³)	Relative Density (%)	Theoretical Density (g/cm ³)
hot-pressed ceramics	4.2205	97.15	
hot-formed ceramics ($\Delta a = 51\%$)	4.3172	99.37	4.3441
Single crystal	4.3039	99.07	

Figure 4 shows the transmittance spectra of Nd³⁺, Y³⁺: SrF₂ single crystal, hot-formed ceramics with different deformation rate, and hot-pressed ceramics by sintering nanopowders, in the wavelength range from 200 to 1200 nm. It can be clearly seen that the transmittance of the hot-formed ceramics is nearly similar to the single crystal with same component, even though with different deformation rate. The transmittance of all the hot-formed ceramics were higher than 85% between 200 and 1200 nm. At the wavelength of 1054 nm, the transmittance of the hot-formed ceramics reached 90%, which is beneficial for the laser pumping. It also indicates that the deformation rate had little effect on the transmittance of the ceramics. Compared with the single crystal and hot-formed ceramics, the hot-pressed ceramics by sintering nanopowders shows worse transmittance (lower than 80%) in the wavelength range from 200 to 1200 nm. This phenomenon can be explained as follows: when light passed through the hot-pressed ceramic, the pores within the microstructure caused strong scattering centers [27,28]. It is reported that during the sintering process, pores exist more easily in the ceramics, leading to lower relative density [29], which is consistent with the measured results shown in Table 2. Meanwhile, in Figure 4, the absorption peaks were located at the wavelength of 352, 427, 466, 521, 576, 625, 675, 735, 796, and 865 nm, which correspond to the transitions of Nd ions from the ground state ${}^{4}I^{9/2}$ to ${}^{4}F_{5/2}$ + ${}^{2}H_{9/2}, {}^{4}F_{7/2} + {}^{4}S_{3/2}, {}^{4}F_{9/2}, {}^{4}G_{5/2} + {}^{2}G_{7/2}, {}^{2}K_{13/2} + {}^{4}G_{9/2}, {}^{2}K_{15/2} + {}^{2}D_{3/2} + {}^{4}G_{11/2}, {}^{4}G_{7/2}, {}^{2}G_{9/2}, {}^{2}P_{2/3}, {}^{4}D_{3/2}, {}^{4}D_{3/2} + {}^{4}G_{11/2}, {}^$ ${}^{4}D_{2/5} + {}^{2}I_{11/2} + {}^{4}D_{1/2}$, ${}^{2}L_{15/2} + {}^{4}D_{7/2}$ and ${}^{4}F_{3/2}$ excited multiplets.



Figure 4. Transmittance spectra of the Nd^{3+} , Y^{3+} : SrF_2 single crystal, hot-pressed ceramics, and hot-formed ceramics with different deformation rate.

Figure 5 shows the laser oscillatory spectra of Nd³⁺, Y³⁺: SrF₂ single crystal and hot-formed ceramics ($\Delta a = 51\%$) under 796 nm wavelength LD pump. The center wavelengths of the continuous laser spectra were almost same, and were both located at 1053 nm. The intensity of output peak of the single crystal and hot-formed ceramic were nearly same, but the FWHM of the hot-formed ceramic (FWHM = 2.55 nm) is larger than that of the single crystal (FWHM = 1.55 nm), which is more suitable for the application as ultrafast and tunable lasers [30].



Figure 5. Laser oscillatory spectra of the Nd³⁺, Y³⁺: SrF₂ single crystal and hot-formed ceramics ($\Delta a = 51\%$) under 796 nm wavelength laser diode (LD) pump.

The thermal conductivities of the Nd³⁺, Y³⁺: SrF₂ single crystal and hot-formed ceramics ($\Delta a = 51\%$) were measured over a temperature range from 50 to 300 °C, as shown in Figure 6. It is clearly revealed that the thermal conductivity of the hot-formed ceramics and single crystal decreased as the temperature increased, which is attributed to the decrease in intrinsic phonons scattering with the increase in test temperature [31]. This has also been confirmed in system of CaF₂ [32] and LiF ceramics [33]. Furthermore, the thermal conductivity value of a single crystal is slightly higher than that of the hot-formed ceramics ($\Delta a = 51\%$) within the testing temperature range. This change can be assigned to the increase in both temperature and pressure, the structure of single crystal transferred is into the layered structure, and grain boundaries were formed, which causes the phonon scattering to increase, resulting in the decrease of the mean free path of phonons. Then, the thermal conductivity decreased, though this difference has little effect on the optical properties of the hot-formed ceramics.



Figure 6. Thermal conductivities of the Nd³⁺, Y³⁺: SrF₂ single crystal and hot-formed ceramics ($\Delta a = 51\%$) vs. the testing temperature.

4. Conclusions

Nd³⁺, Y³⁺: SrF₂ transparent ceramics were successfully synthesized by hot-forming and hot-pressing techniques. The SEM images of the fracture surface shows that a few residual pores existed between the grains of hot-pressed ceramics, and the hot-formed ceramic exhibited a series of layered structure. The hot-pressed ceramics possessed excellent mechanical property but low density, worse transmittance, and failed to achieve laser output compared with hot-formed ceramic and a single crystal. The hot-formed ceramics exhibited good mechanical property and laser performance than those of single crystals. The effects of deformation rate of the single crystal on the optical and mechanical properties of laser ceramics were studied. The transmittance of Nd³⁺, Y³⁺: SrF₂ hot-formed ceramics at different deformation rates were similar to the single crystal. The hot-formed ceramics at the deformation rate of 51% exhibited best microhardness (H = 2.570 GPa) and fracture toughness (K_{1C} = 0.70 MPa m^{1/2}) compared to single crystal and hot-formed ceramics at other deformation rate of single crystal and hot-formed ceramics at other deformation rate of the hot-formed ceramics. The FWHM of the hot-formed ceramic (FWHM = 2.55 nm) was larger than that of the single crystal (FWHM = 1.55 nm) in CW laser operation, which revealed that the hot-formed ceramics are a type of promising material for high-power laser devices.

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